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# Recovery of cobalt and copper from single- and co-contaminated simulated electroplating wastewater via carbonate and hydroxide precipitation

Khyle Glainmer N. Quiton<sup>1</sup>, Yao-Hui Huang<sup>1,2\*</sup> and Ming-Chun Lu<sup>3</sup>

## Abstract

Wastewater containing cobalt and copper comprised of plating wash water, plant wash water, and equipment cooling and wash water is generated in the electroplating industry. These metals can be detrimental to humans, animals, plants, and the environment. Thus, it is necessary to treat electroplating wastewater to remove these toxic metals. Carbonate and hydroxide precipitation were utilized for the removal of Co (II) and Cu (II) from synthetic electroplating wastewater by jar tests in this work. The effects of solution pH, precipitant-to-metal ratio, and type of precipitant on the precipitation efficiency of cobalt and copper from the single- and co-contaminated systems were investigated. Carbonate precipitation achieved higher removal efficiency for both target metals in the single- and co-contaminated wastewater streams. Furthermore, it can operate at relatively low pH range of about 7–8. Cobalt in both pollutant systems was almost completely removed at pH 10 using both precipitant systems. Copper was found to be easily removed which was possibly brought about by precipitation-adsorption mechanism. The extent of the co-removal of cobalt with copper is significantly pH dependent. The effect of precipitant-to-metal ratio for cobalt and copper treatment varied in single- and co-contaminated streams. Carbonate precipitation led to higher sludge volume than that of hydroxide precipitation.

**Keywords:** Chemical precipitation, Cobalt removal, Copper system, Hydroxide precipitation, Wastewater stream

## 1 Introduction

With the progressing economy, and rapid growth and development of industries including mining and smelting operations, leather tanning, metal plating facilities, metal cleaning and fabrication, metal finishing, battery manufacturing, electrochemical, paint and pigment industries, heavy metals are being discharged into the aquatic streams to an increasing degree [1]. These recalcitrant and persistent pollutants are considered to be toxic,

carcinogenic, and non-biodegradable which pose detrimental effects on biological environment and human health [2]. Thus, remediation of these contaminants in water and wastewater (WW) has been of particular concern.

Cobalt is a significant cofactor in Vitamin B12 responsible for the proper functioning of the brain and nervous system, and for blood formation. It is one of the most essential transition metals beneficial to human beings. However, excessive intake may be hazardous to both humans and animals. Moreover, exposure to high levels of cobalt may induce toxic effects and may cause goiter, thyroid damage, diarrhea, nausea, reproductive problems, hypertension, heart disease, bleeding, pulmonary

\*Correspondence: [yhhuang@mail.ncku.edu.tw](mailto:yhhuang@mail.ncku.edu.tw)

<sup>2</sup> Sustainable Environment Research Center, National Cheng Kung University, Tainan 70101, Taiwan  
Full list of author information is available at the end of the article



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diseases, hyperglycemia, hair loss, bone defects, and mutations in living cells [3, 4]. With this, cobalt concentration in livestock wastewater and irrigation water should not exceed 1.0 and 0.05 mgL<sup>-1</sup>, respectively, as set in the Canadian Water Quality Guidelines. In addition, Taiwan has set an effluent standard of 1 mgL<sup>-1</sup> for cobalt [3]. On the other hand, copper is another beneficial metal ion present as trace amounts in our body and water resources. It regulates hemoglobin level, neuron action, mitochondrial respiration, and metabolism by cells. At higher concentrations, liver and kidneys can be affected to a great extent. Its accumulation can cause diseases such as anemia, Alzheimer's disease, and Parkinson's disease [4, 5]. The permissible limits of copper in drinking water (World Health Organization) and effluent discharge (United States Environmental Protection Agency) are set to 0.0015 and 1.3 mgL<sup>-1</sup>, respectively [6, 7]. These heavy metals may cause short- and long-term toxicological effects on human health. Thus, numerous techniques have been studied and applied for the remediation of these pollutants [8]. At present, chemical precipitation, coagulation/flocculation, electrochemical method, ion exchange, membrane filtration and adsorption are the existing treatment technologies to remove heavy metals in water and wastewater streams [9, 10]. Among these current methods, chemical precipitation is the most widely utilized method in the industry particularly due to the simplicity of process control, effectivity over a wide range of temperature and relatively low operating cost [9, 11]. Traditionally, chemical precipitation processes produce insoluble precipitates of heavy metals in the form of hydroxides, sulfides, carbonates, and phosphates. Chemical precipitation mechanism involves the reaction of dissolved metals in the solution with the precipitating agent producing insoluble metal precipitates. Consequently, very fine particles are generated, and their particle size can increase by using chemical precipitants, coagulants, and flocculation leading to their removal as sludge. Once the metals precipitate leading to the formation of solids, they can easily be removed, and low metal concentrations can consequently be released. Removal efficiency of metal ions in the solution can reach optimum by changing the significant parameters including pH, temperature, initial metal concentration, and charge of the ions (via charge neutralization) [12]. Chemical precipitation process usually involves addition of reagents, pH adjustment inducing precipitation, flocculation, sedimentation and solid-liquid separation [11]. Oftentimes, alkaline reagents are utilized to raise the pH of the solution lowering the solubility of the metallic constituent, consequently leading to precipitation. It includes sulfide, hydroxide and carbonate precipitation [13]. Operating costs for

hydroxide and carbonate precipitation processes are almost similar. They are of lower cost than sulfide precipitation [14].

Hydroxide precipitation removes heavy metals by the addition of alkalis (caustic or lime) to adjust the pH of the wastewater until the pollutant metal exhibits its minimum solubility. It is easy to operate, operates at ambient conditions, and appropriate for automatic control. The most significant advantage of this process is its low cost [15]. On the other hand, carbonate precipitation using sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) is a low-cost chemical precipitation process with added advantages such as its simplicity, optimum treatment occurring at less pH levels and sludges with good filtration characteristics [11].

Few investigations have utilized chemical precipitation method in treating co-contaminated heavy metal wastewater streams, particularly containing cobalt and copper [2, 16]. Thus, the aim of the study is to investigate the influence of pH, precipitant-to-metal ratio, and type of precipitant on the co-removal of cobalt with copper from synthetic electroplating wastewater using carbonate and hydroxide precipitating agents since these pollutants co-exist in the said wastewater stream. Single-contaminated synthetic wastewater was also treated for comparison in terms of removal efficiency, and sludge volume generation.

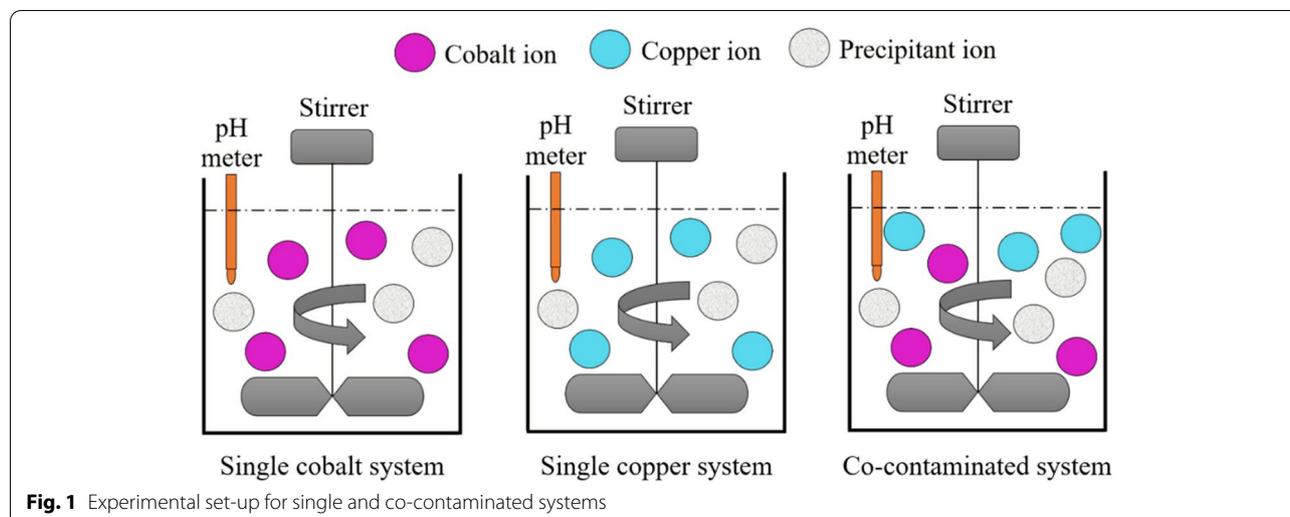
## 2 Materials and methods

### 2.1 Chemicals

All reagents were of analytical grade and used without further purification. Cobalt sulfate heptahydrate (99%) was purchased from Sigma-Aldrich (China). Copper sulfate pentahydrate (≥ 98.5%) and sodium carbonate (≥ 99.5%) were provided by Fluka (Switzerland). Sodium hydroxide (NaOH, ≥ 97%) was obtained from Fisher Chemical (UK). Nitric acid (HNO<sub>3</sub>) was purchased from Shimadzu's Pure Chemicals (Japan). A laboratory-grade RO-ultrapure water system (resistance > 18.1 Ω) supplied deionized water for the experiments.

### 2.2 Batch experiments

Single-contaminated aqueous solutions of cobalt and copper with 12.6 mM concentration were prepared as well as co-contaminated aqueous stream where initial concentration of each metal was 12.6 mM where the molar ratio of Co to Cu is 1:1. The actual concentrations of cobalt and copper in the real WW range from about 3 to 1500 mgL<sup>-1</sup> [17, 18]. Thus, the concentration used in this study was 12.6 mM (800 mgL<sup>-1</sup>) which is in the range of the actual electroplating WW. Batch experiments of chemical precipitation were conducted by jar tests as shown in Fig. 1 at different pH levels of 7, 8, 9, 10, 11, and 12, and precipitant-to-metal ratios ([P]/[M]) of



0.5, 1.0, 1.5, 2.0, and 2.5. All the experimental runs were carried out at room temperature. Na<sub>2</sub>CO<sub>3</sub> and NaOH were used for carbonate and hydroxide precipitant precursors, respectively, to determine the effect of precipitants on the treatment of single- and co-contaminated streams. The mixture was stirred at 100rpm for 10min then 30rpm for 50min as adapted from the literature [19], and finally kept for settling to draw liquid sample for residual cobalt and copper analysis. For the cobalt and copper residue, the supernatant liquid was filtered with 0.22 μm syringe filter and digested with 1 mL HNO<sub>3</sub> (70%) to stop precipitation.

### 2.3 Analytical methods

Volumetric method was used to determine the estimated volume of the decanted sludge. The sludge volume at 30 min (SV<sub>30</sub>) was determined using an Imhoff cone (Kartell Labware, Italy). The sludge settling rate (SSR, cm<sup>3</sup> min<sup>-1</sup>) was determined in the reaction system given by Eq. (1). Cobalt and copper residues were measured by using inductively coupled plasma mass spectrometry (JY 2000-2, HORIDA).

$$\text{Sludge settling rate, SSR} \left( \frac{\text{cm}^3}{\text{min}} \right) = \frac{V_{\text{sol'n}} - SV_{30}}{t_s} \tag{1}$$

where V<sub>sol'n</sub> is total volume of the solution (cm<sup>3</sup>), SV<sub>30</sub> is the sludge volume at 30 min (cm<sup>3</sup>) and t<sub>s</sub> is the settling time (30 min). X-ray diffraction (XRD, DX III, Rigaku, Japan) was utilized to analyze the crystallinity of the precipitates. The chemical surface composition was determined using Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet 6700, USA). An energy

dispersive spectroscopy (EDS, INCA400, OXFORD) was used to observe the elemental components of the solid samples.

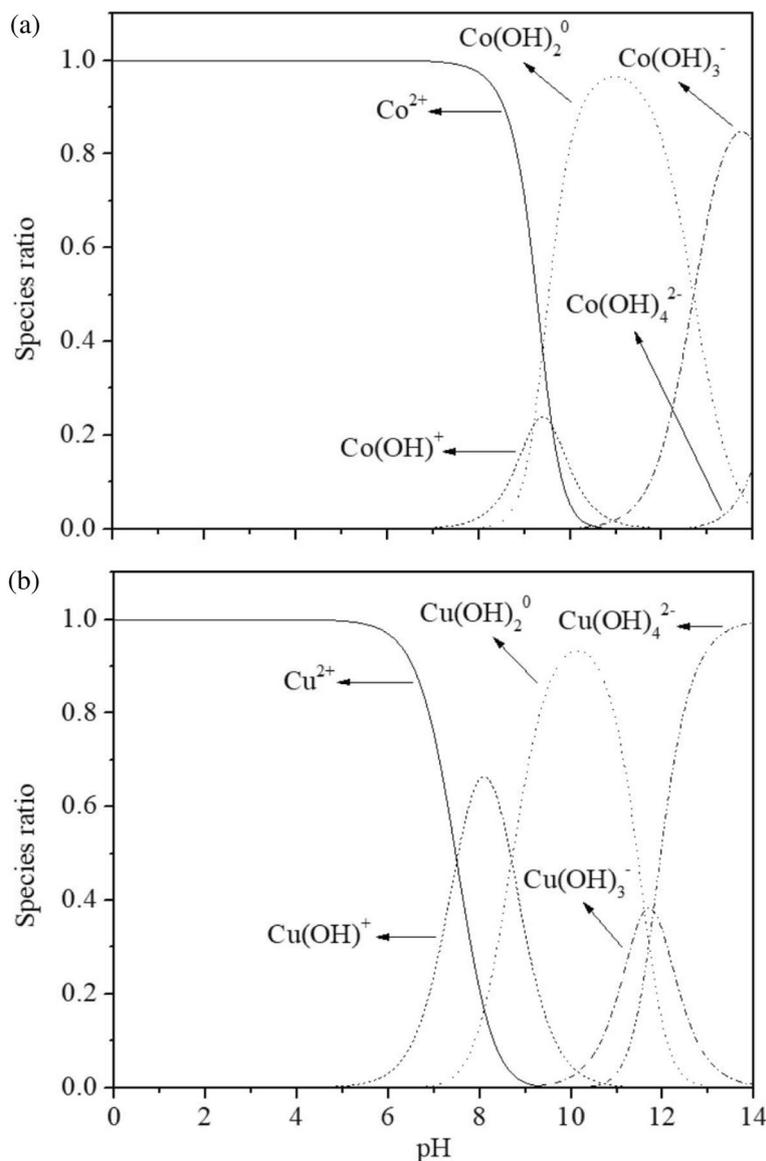
## 3 Results and discussion

### 3.1 Cobalt and copper speciation

The treatability of Co and Cu via chemical precipitation in waste abatement applications is directly related to their solubilities in the solvent matrix. Their solubility profiles can be altered by one or more of the following process modifications: (1) controlling the temperature of an aqueous solution, (2) adjusting the pH and reduction potential of the solution, or (3) setting supersaturation by increasing or decreasing the concentration of solute in a fixed-volume solution (constant volume) [20, 21].

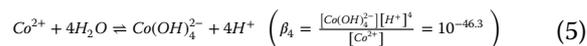
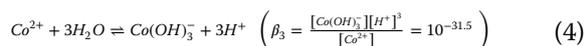
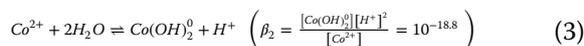
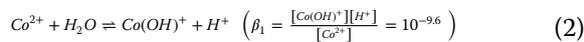
#### 3.1.1 Cobalt speciation

Figure 2a displays the distribution of soluble species of individual hydroxo Co<sup>2+</sup> complexes. These hydro complexes always exist in water while different anions can form complexes with cobaltous ion based on stability constants. Common anions include SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. These complexes form precipitates when the solubility product is surpassed [22]. Cobaltous ions, Co<sup>2+</sup>, exist in acid and weak alkaline solutions depending on the extent of cobalt concentration. Increasing the pH will allow Co<sup>2+</sup> to react with OH<sup>-</sup> ions forming cobaltous hydroxide, Co(OH)<sub>2</sub>. Nevertheless, the Co(OH)<sub>2</sub> precipitate may undergo redissolution into dicobaltite ions, HCoO<sub>2</sub><sup>-</sup>, when the pH reaches greater than 13.4. Hydrolysis products of Co<sup>2+</sup> are summarized varying from Co(OH)<sup>+</sup> to Co(OH)<sub>4</sub><sup>2-</sup> [23] as indicated in Eqs. (2) to (5) together with their



**Fig. 2** Speciation of (a) cobalt and (b) copper for soluble hydro complexes in pure water [22]

respective solubility products. These hydroxyl species in different forms appear at a pH level above 8.



The total cobalt in water can be presented as

$$[Co]_T = [Co^{2+}] + [Co(OH)^+] + [Co(OH)_2^0] + [Co(OH)_3^-] + [Co(OH)_4^{2-}] \quad (6)$$

Factoring out  $[Co^{2+}]$  and substituting Eqs. (2) to (5), Eq. (6) will be depicted as Eq. (7) and then simplified into Eq. (8). Equation (8) is consequently rearranged as Eq. (9) to determine the value of  $[Co^{2+}]$ .

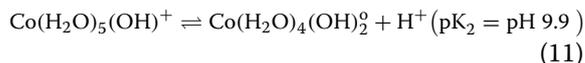
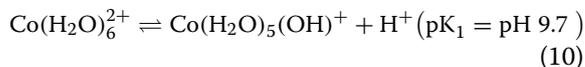
$$[Co]_T = [Co^{2+}] \left( 1 + \frac{\beta_1}{[H^+]} + \frac{\beta_2}{[H^+]^2} + \frac{\beta_3}{[H^+]^3} + \frac{\beta_4}{[H^+]^4} \right) \tag{7}$$

$$[Co]_T = [Co^{2+}] \cdot \alpha_{Co} \tag{8}$$

$$[Co^{2+}] = \frac{[Co]_T}{\alpha_{Co}}$$

As depicted in Fig. 2a,  $Co^{2+}$  is the dominating species until pH8 and the sharply decreases as the pH increases. Subsequently,  $Co(OH)^+$  starts to appear at this pH level and reaches a maximum at around pH9.5. Amongst the hydrolysis products,  $Co(OH)_2^o$  can be considered as the most significant leading to  $Co(OH)_2$  precipitation. Similarly, Fig. 3a shows that cobalt chemistry is predominately controlled

by its  $Co^{2+}$  oxidation state at ambient conditions [21]. The  $Co^{3+}$  oxidation state can only exist if a strong chelating organic molecule is complexed in aqueous solution due to its notably low solubility ( $K_{sp}$  of  $Co(OH)_3 = 10^{-44.5}$ ;  $K_{sp}$  of  $CoOOH = 10^{-50.0}$ ) [24].  $Co^{2+}$  can be coordinated octahedrally with six water molecules in the form of  $Co(H_2O)_6^{2+}$ . This cation can undergo hydrolysis as shown below.



At typical pH values of 4 to 8, the hydrolysis species concentrations will be relatively 2 to 6 magnitude orders lower than the  $Co(H_2O)_6^{2+}$  species. When the

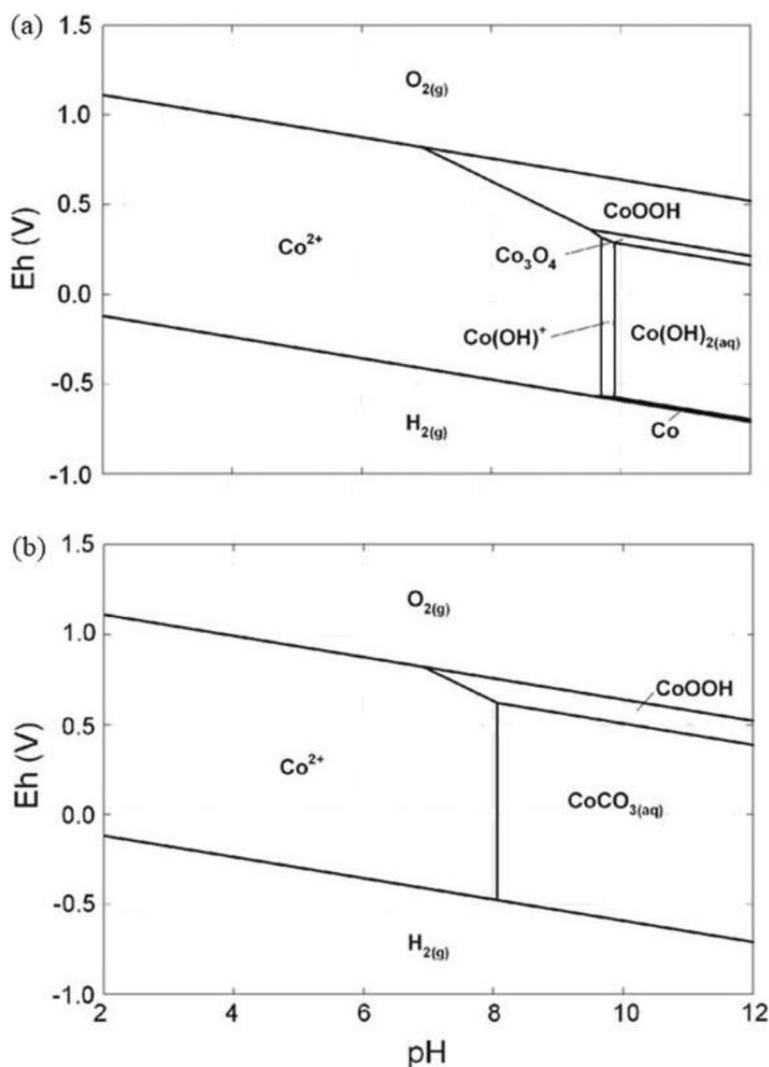
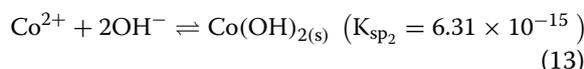
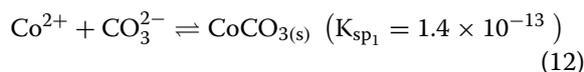


Fig. 3 Pourbaix diagram of cobalt in (a) closed and (b) open systems [21]

system is exposed in the ambient atmosphere, the complexation of cobalt by carbonate becomes more significant as shown in Fig. 3b. Furthermore, Table 1 reports the different inorganic cobalt species with the corresponding stability constants [25]. Carbonate and hydroxyl anions react with cobalt cation to form  $\text{CoCO}_3$ ,  $\text{Co(OH)}_2$ , or cobalt hydroxide carbonate as shown in Eqs. (12) and (13) [26]. In this case, cobalt hydroxide shows lesser solubility indicated in its smaller solubility product constant which pertains to higher probability of precipitation in the system compared to that of cobalt carbonate.



Applying the viewpoint of  $K_{sp}$  and the equilibrium of water ionization, we can calculate the necessary concentration of precipitant anions required for the formation of  $\text{Co(OH)}_2$  and  $\text{CoCO}_3$  precipitates presented in Eqs. (14) and (15), respectively:

$$[\text{OH}^-] = \sqrt{\frac{K_{sp}(\text{Co(OH)}_2)}{[\text{Co}^{2+}]}} \quad (14)$$

$$[\text{CO}_3^{2-}] = \frac{K_{sp}(\text{CoCO}_3)}{[\text{Co}^{2+}]} \quad (15)$$

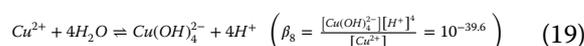
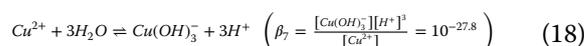
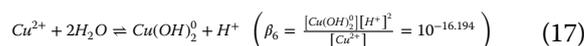
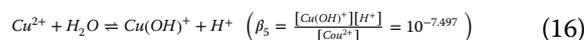
We apply 12.6mM as the concentration of  $\text{Co}^{2+}$  used in this study to determine the precipitant anion concentration. Thus,  $7.08 \times 10^{-7}$  M of  $\text{OH}^-$  is needed to obtain  $\text{Co(OH)}_2$  precipitate. Whereas  $1.11 \times 10^{-11}$  M of  $\text{CO}_3^{2-}$  is sufficed to produce  $\text{CoCO}_3$  in the system.

**Table 1** Homogeneous and heterogeneous equilibria of inorganic  $\text{Co}^{2+}$  in aqueous medium

Equilibria	log K
$\text{Co}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CoOH}^+ + \text{H}^+$	-9.6
$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_2^0 + \text{H}^+$	-18.8
$\text{Co}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CoCO}_3^0$	3.17
$\text{Co}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CoHCO}_3^+$	1.39
$\text{Co}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CoHCO}_3^+$	1.39
$\text{Co}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CoSO}_4^0$	2.36
$\text{Co}^{2+} + \text{Cl}^- \rightleftharpoons \text{CoCl}^+$	-0.05
$\text{CoO}_{(s)} + \text{H}_2\text{O} \rightleftharpoons \text{Co}^{2+} + 2\text{OH}^-$	-14.87
$\text{CoCO}_{3(s)} + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + \text{CO}_{2(g)} + \text{H}_2\text{O}$	10.35
$\text{CoCO}_{3(s)} \rightleftharpoons \text{Co}^{2+} + \text{CO}_3^{2-}$	-9.52

### 3.1.2 Copper speciation

Like cobalt and other metals, copper interacting with water, forms free metal cations, different soluble complexes and insoluble particles or precipitates. Free copper, which is cupric ion ( $\text{Cu}^{2+}$ ), is generally soluble and the preferential form at relatively low degree of pH (usually below pH6) as shown in Fig. 2b and in the absence of anionic ligands [22]. As presented,  $\text{Cu}^{2+}$  is the most dominant species (greater than 80%) when the pH is 6 but its relative dominance decreased quickly as pH increased [22]. Soluble copper hydro complexes are formed at low and high pH range in pure water and given by the reactions below depicted as Eqs. (16) to (19). In the presence of anionic ligands, these complexes form precipitates such as  $\text{Cu(OH)}_2$ ,  $\text{CuCO}_3$ , etc.



In pure water, the total copper can be depicted as follows:

$$[\text{Cu}]_T = [\text{Cu}^{2+}] + [\text{Cu(OH)}^+] + [\text{Cu(OH)}_2^0] + [\text{Cu(OH)}_3^-] + [\text{Cu(OH)}_4^{2-}] \quad (20)$$

Substituting Eqs. (16) to (19), the total copper is presented as

$$[\text{Cu}]_T = [\text{Cu}^{2+}] \left( 1 + \frac{\beta_5}{[\text{H}^+]} + \frac{\beta_6}{[\text{H}^+]^2} + \frac{\beta_7}{[\text{H}^+]^3} + \frac{\beta_8}{[\text{H}^+]^4} \right) \quad (21)$$

$$[\text{Cu}]_T = [\text{Cu}^{2+}] \cdot \alpha_{\text{Cu}} \quad (22)$$

Thus, the value of  $[\text{Cu}^{2+}]$  is

$$[\text{Cu}^{2+}] = \frac{[\text{Cu}]_T}{\alpha_{\text{Cu}}} \quad (23)$$

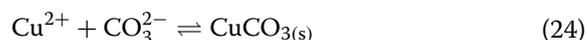
### 3.2 Effect of pH

The effect of pH on the removal of cobalt and copper in the single- and co-contaminated systems was studied from pH levels of 7–12 treating 12.6mM initial metal concentration and precipitant-to-metal ratio of 1.2 in 1 h of reaction time in a batch system. pH indicates the concentration of hydrogen ions ( $\text{H}^+$ ) in the solution and controls the molecular net electric charge to alter

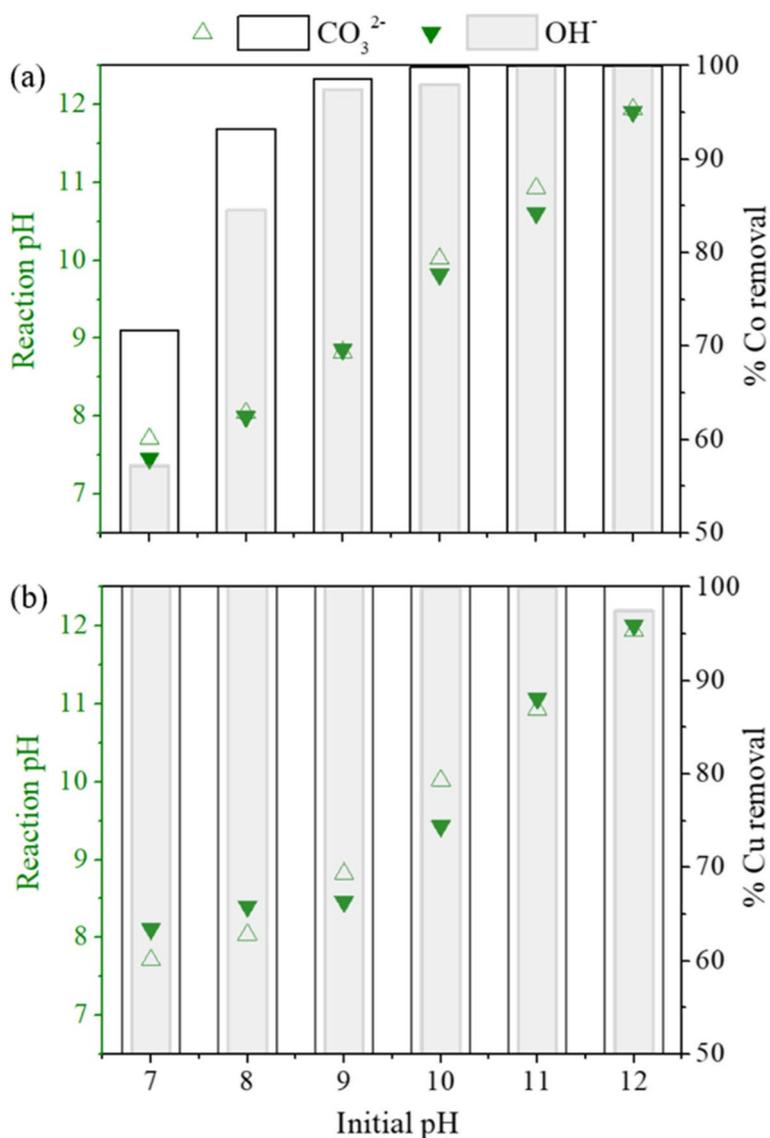
the mobility of a known substance in the water matrix. A heavy metal with relatively low mobility, being insoluble, has a negative net charge ( $H^+$  depletion) leading to precipitation out of the liquid phase. Generally, this phenomenon takes place in high pH zones and is usually termed as alkaline precipitation. Contrarily, a metal exhibiting high mobility (soluble) has a net positive charge caused by  $H^+$  supplementation in the solution, consequently resulting to aqueous dissolution of metals in acidic environments [27]. Furthermore, the pH value of the reaction directly influences the concentration of carbonate ions in the reaction system, and then influences nucleation and growth of the crystalline precipitation during the treatment process [26]. Thus, pH is a relatively significant variable with regards to this process under investigation. The influence of pH on the behavior of cobalt in the single synthetic solution is presented in Fig. 4a. At pH7, 72% removal was reached by carbonate precipitation while hydroxide precipitation brought about 59% removal leading to residual cobalt of 3.6 and 5.2 mM, respectively. At pH9, the removal efficiency significantly increased using the carbonate and hydroxide precipitants achieving almost complete removal. At pH11, the highest removal of cobalt (100%) was attained for both studied precipitants conforming to the standard set by Canada and Taiwan ( $1\text{ mg L}^{-1}$  for both livestock WW and effluent) for cobalt. 100% cobalt removal was also achieved at pH values of 8 to 10 owing to  $Co(OH)_2$  precipitation [28].  $CoCO_3$  and  $Co(OH)_3$  can be produced in an acidic and strong alkaline solution, respectively, in a carbonate or bicarbonate system.  $Co(OH)_2$  is usually formed in strong alkaline solution [28]. In this present study, it was concluded that cobalt removal increased with increasing solution pH. Qasem et al. [29] affirmed that, in general, metal precipitation process efficiency is improved at higher pH range from 9 to 11.

The generated sludge volume at 30 min by the single cobalt system was observed to determine the settleability of the sludge at different pH values under identical operating conditions depicted in Fig. 5a. For cobalt removal under carbonate precipitation, the remaining sludge volume was found to increase when pH increased from 7 to 11 and decreased significantly at pH12. This shows that the sludge particles have higher settleability when the pH approaches neutral condition causing faster settling rate as presented in Fig. 5b. Likely cobalt carbonate exists at pH7 showing significant decrease in the settleability from pH8.  $CoCO_3$  occurs at pH range of 6.9 to 7.5 as reported by Guo et al. [30]. The cobalt precipitate formed at pH11 was observed to be black in color probably due to  $Co_3O_4$  precipitation. Whilst at pH12, brown precipitate was recovered which can be attributed to  $CoOOH$

precipitation [31]. However, the XRD analyses show that the cobalt precipitates under carbonate system were of amorphous in nature (Fig. 6a and b). The change in cobalt species at different pH levels is possibly caused by oxidation [32]. For cobalt removal under hydroxide precipitation, there was a great increase in the sludge volume from pH8 to 9. A decreasing sludge volume was then observed from pH9 to 12. The XRD patterns varying the pH values for hydroxide precipitation would fit on the  $Co(OH)_2$  crystal peaks (JCPD #30-0443) as presented in Fig. 6 c and d. The changes in the sludge volume could be attributed to the particle size and particle density as divulged by Lacson et al. [33]. On the other hand, copper was easily removed using both carbonate and hydroxide systems as described in Fig. 4b. Precipitation reactions of copper are shown below:



The  $[CO_3^{2-}]/[Cu^{2+}]$  ratio used in this study is 1.2 which is in excess with the required carbonate based on the stoichiometric reaction presented in Eq. (24). The excess carbonate used possibly caused the high removal efficiency of the copper in the single system. This was possibly brought about by greater amount of carbonate ions interacting with the target copper ions. In addition, precipitation starts at pH6 and all copper was precipitated out at pH7 for pure copper solution with  $150\text{ mg L}^{-1}$  of concentration [34]. A cationic metal is generally mostly dissolved at relatively low pH and becomes mostly adsorbed at higher pH values as pH increases through a critical range 1–2 pH units wide. The high removal obtained in this system is also probably due to precipitation and adsorption mechanisms most especially at higher pH levels. Copper possibly formed copper-bearing precipitates initially and the remaining copper in the solution was adsorbed on the surface of the precipitates formed in the system causing no residual copper left in the solution [35]. This occurrence could be due to electrostatic attraction [36, 37]. Furthermore, copper carbonate precipitates are known to have appreciable amount of positive surface charges ascribed to high level of particles' zeta potential. When the solution pH is gradually elevated, these positive surface charges are suddenly reduced and finally shifted to negative surface charge when the pH reaches higher than 7.5 [34]. This explains the possible phenomenon occurring in the single copper system using carbonate precipitation. At pH12, there was an observed decrease in the removal of copper using hydroxide which is probably caused by the re-dissolution of the precipitate

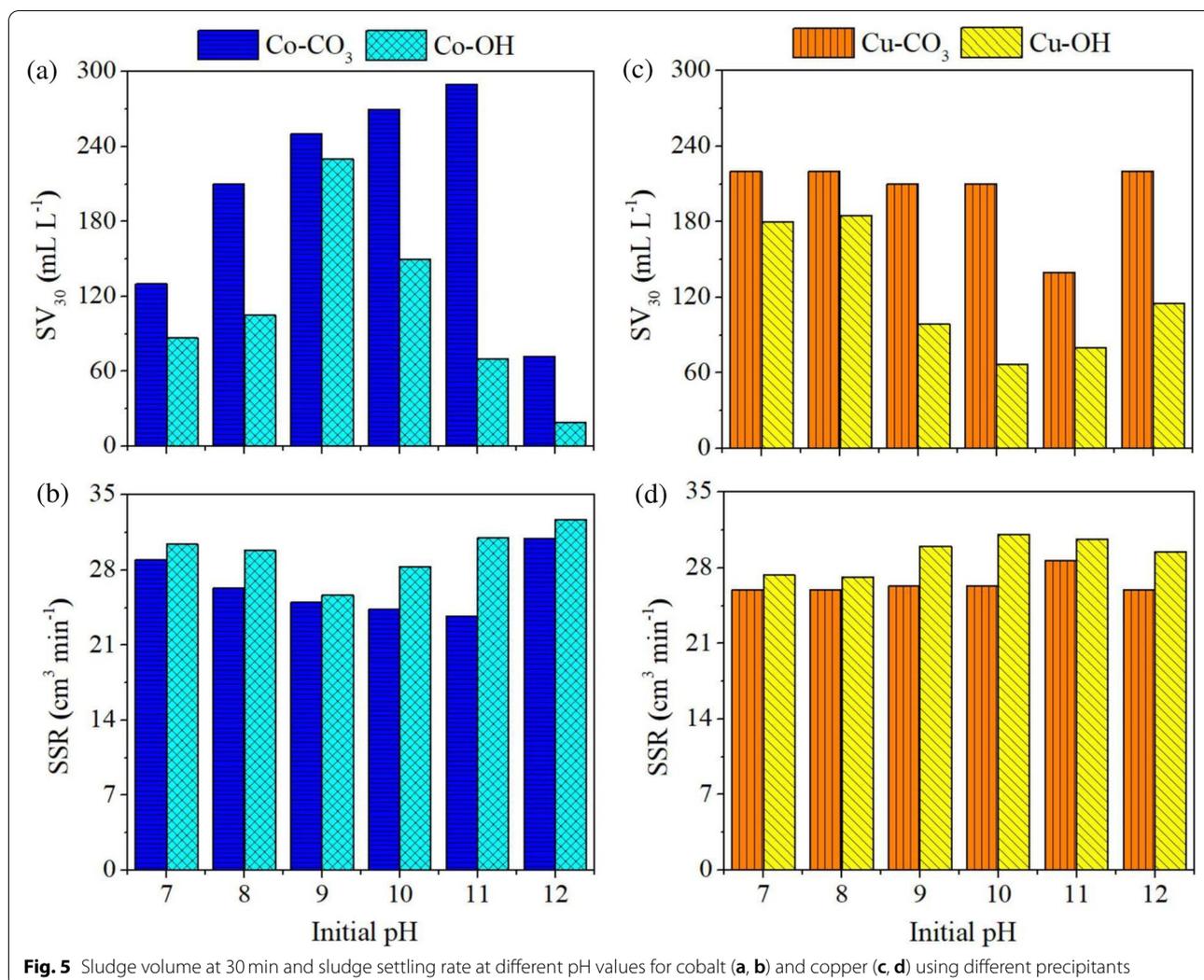


**Fig. 4** Removal efficiency of (a) cobalt and (b) copper at different pH values using different precipitants (Conditions:  $[\text{Co}]_0 = [\text{Cu}]_0 = 12.6 \text{ mM}$ ;  $\text{pH} = \text{variable}$ ;  $[\text{P}]/[\text{M}] = 1.2$ )

in the solution and/or desorption of copper from the copper-bearing precipitate. With respect to the stoichiometry of the reaction shown in Eq. (25), the required  $[\text{OH}^-]/[\text{Cu}^{2+}]$  molar ratio represents a hydroxide concentration 60% below the stoichiometric requirement which is affected by pH inducing copper precipitation. Similar results were obtained when hydroxide precipitation was used to treat single copper system reaching greater than 97% removal.

For carbonate precipitation,  $\text{SV}_{30}$  ranges from about 140 to 220 mL per liter of mixed copper and precipitant solution while about 70 to 180 mL per liter was

observed for hydroxide precipitation as depicted in Fig. 5c. Malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , dominates in the copper solution at pH between 7 and 8. It was also observed by Sanchez et al. [38] that malachite exists at pH up to 10.3. This could explain the similar sludge volume generated from pH values of 7 to 10 in the single copper system. As depicted in Fig. 7a, the XRD pattern for the copper precipitate at pH 7 shows the characteristic peaks of malachite confirming its existence at this pH level (JCPD #41-1390). At pH 11, the  $\text{SV}_{30}$  significantly decreased possibly due to azurite formation. Azurite has higher molecular weight than malachite



**Fig. 5** Sludge volume at 30 min and sludge settling rate at different pH values for cobalt (a, b) and copper (c, d) using different precipitants

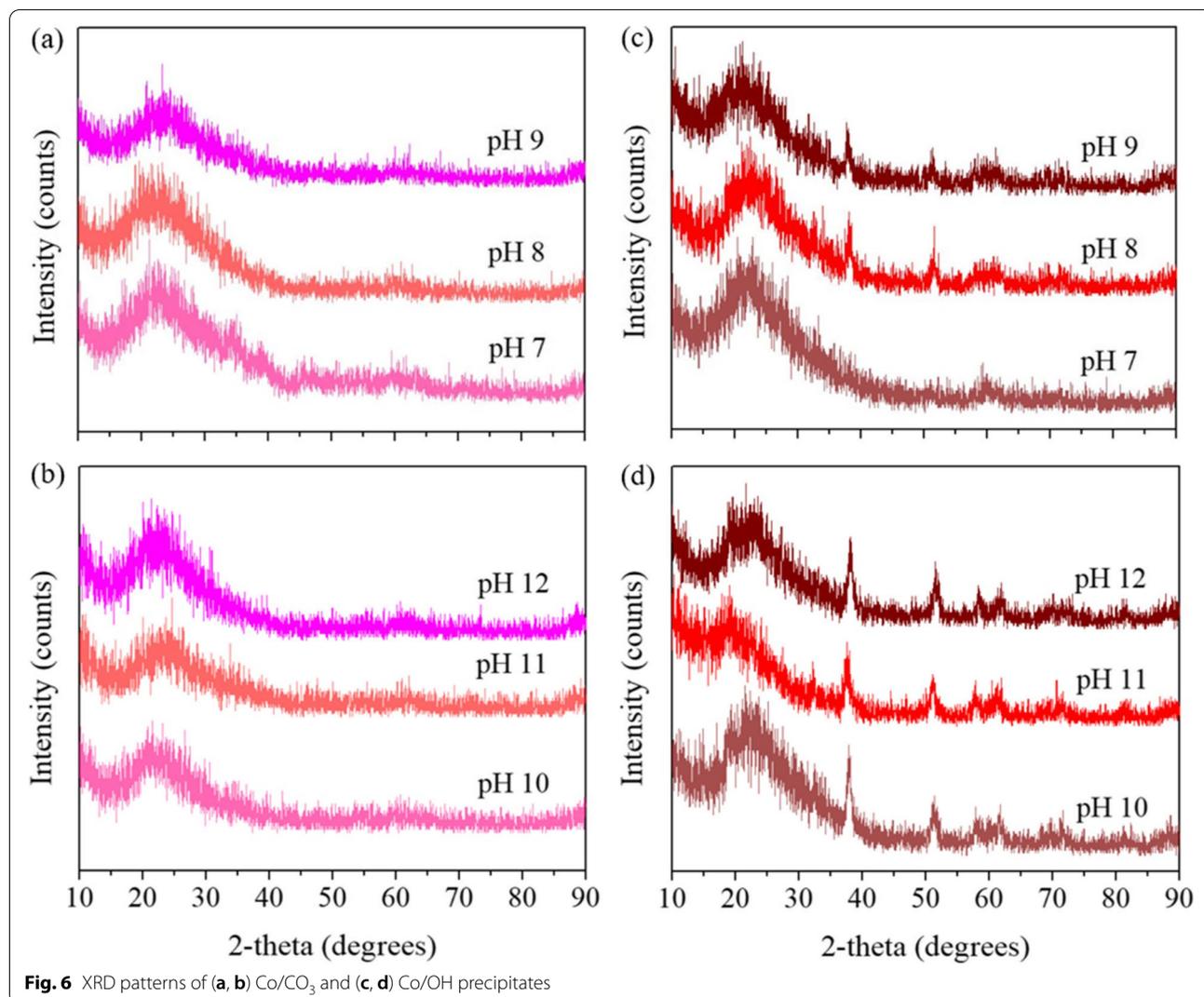
which corresponds to heavier particles affecting the settleability (faster) as shown in Fig. 5d, thus, leading to decreased sludge volume. At pH values between 6 to 7 and 10.3 to 14, azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , could be the dominating species making it amphoteric. Black precipitate was observed at pH 12 which can be associated with CuO precipitation occurring at  $\text{pH} > 10.3$ . At pH 7 and 8 using hydroxide precipitation,  $\text{Cu}(\text{OH})_2$  is the predicted precipitate which exists at pH values ranging from 5.5 to 10.3 [38]. This precipitate is also said to exist at intermediate pH levels typically in the pH range of 6.5–12 [22]. Minimal solubility of metal hydroxides leading to higher probability of precipitation is achieved at an approximate pH of 9.5–10 [39].  $\text{Cu}(\text{OH})_2$  is possibly formed at pH 9 and 10 exhibiting larger particle size affecting the sludge volume after 30 min. Grayish precipitate was formed at pH 11. From the XRD patterns of all the copper precipitates (Fig. 7 b,

c and d), it was revealed that the samples were crystalline and CuO occurrence was confirmed from the XRD analysis at both pH values of 11 and 12 with JCPD #44–0706 for both precipitants [40]. Characteristic peaks of other impurities including  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}_2\text{O}$  or the precursors used were not observed which indicates the formation of pure CuO phase.

To further validate the results drawn, the solubility products of  $2.20 \times 10^{-20}$  for  $\text{Cu}(\text{OH})_2$  and  $1.40 \times 10^{-10}$  for  $\text{CuCO}_3$  were used to calculate the pH and carbonate concentration for precipitating 12.6 mM  $\text{Cu}^{2+}$  ( $800 \text{ mg L}^{-1}$ ) unto  $\text{Cu}(\text{OH})_2$  and/or  $\text{CuCO}_3$  in an open atmospheric condition.

Precipitation  $\text{Cu}(\text{OH})_2$  and  $\text{CuCO}_3$  occurs when the solubility products are exceeded as shown below.

$$[\text{Cu}^{2+}][\text{OH}^-]^2 = \left(\frac{800}{63.6} \times 10^{-3}\right)(10^{-14+\text{pH}})^2 \geq 10 \times 2.2 \times 10^{-20} \quad (26)$$



$$[Cu^{2+}][CO_3^{2-}] = \left(\frac{800}{63.6} \times 10^{-3}\right)(CO_3^{2-}) \geq 10 \times 1.4 \times 10^{-10} \quad (27)$$

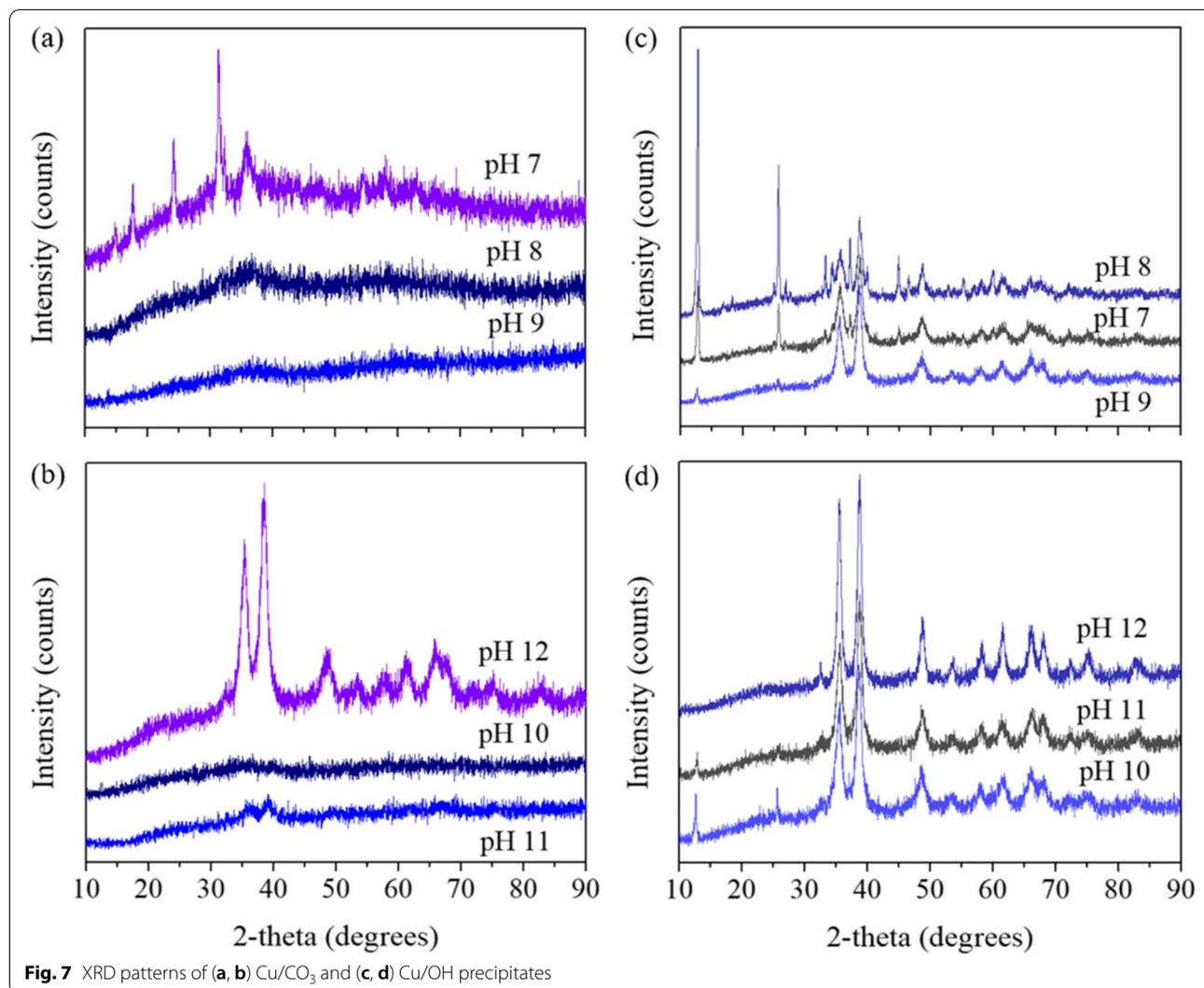
Where 63.6 is the molecular weight of copper (g mol<sup>-1</sup>), 10 is the assumed saturation index for homogeneous precipitation [36, 37],  $2.2 \times 10^{-20}$  is the solubility product of Cu(OH)<sub>2</sub>, and  $1.40 \times 10^{-10}$  is the solubility product of CuCO<sub>3</sub>. Saturation index is the indicator whether water will dissolve or precipitate a particular target, in this case, copper [36, 37].

Thus, pH 5.62 is the theoretical starting pH for Cu(OH)<sub>2</sub> precipitation based from Eq. (26) whereas  $[CO_3^{2-}] \geq 1.11 \times 10^{-7}$  M is the carbonate concentration needed for CuCO<sub>3</sub> precipitation from Eq. (27). Based on Fig. 2b, the pH wherein Cu(OH)<sub>2</sub> starts to appear is pH 7 which agrees with the theoretical starting pH calculated. In an open atmospheric carbonate system, carbonate concentration is given by the equation:

$$[CO_3^{2-}] = \frac{[H_2CO_3^*] \cdot K_{a,1} \cdot K_{a,2}}{[H^+]^2} \quad (28)$$

Where  $[H_2CO_3^*] = [CO_{2(aq)}] = 10^{-5}$  M,  $K_{a,1} = 10^{-6.3}$ , and  $K_{a,2} = 10^{-10.3}$

Substituting all the values and rearranging, we get  $[H^+] \leq 4.76 \times 10^{-8}$ , and pH  $\geq 7.32$ . Thus, the calculations done and analyses suggest that homogeneous copper precipitation of Cu(OH)<sub>2</sub> cannot take place until pH is greater than 5.62 for 12.6 mM Cu<sup>2+</sup> in an open atmospheric condition which is roughly 1.7 pH unit lower than the CuCO<sub>3</sub> precipitation (pH  $\geq 7.32$ ). The results affirm that precipitation occurred at these pH values. However, the actual carbonate concentration (15.12 mM) used in the treatment of copper in the system is four-order of magnitude higher than the calculated value



( $1.11 \times 10^{-3}$  mM). With this, copper could be precipitated at lower pH level compared to cobalt precipitation.

The behavior of Co(II) in the co-contaminated system was also studied in terms of the effect of pH on its removal in the presence of Cu(II) as presented in Fig. 8a. For both precipitants, increasing the pH increased the cobalt co-removal and co-precipitation with copper. Using sodium carbonate as precipitant, cobalt was removed to over 99% at pH9. The same result was achieved by Safitri et al. [41] in treating cobalt in a multi-component heavy metal system reaching over 99% removal at pH9. As shown in Fig. 8a, the optimum pH for maximum cobalt co-removal in the system is about pH10 for both precipitants utilized similar with the results in the single cobalt system (Fig. 4a). The co-removal and co-precipitation of cobalt with copper was found to be greatly dependent on pH similar as the result presented by Sun et al. [37]. The co-removal of chromium

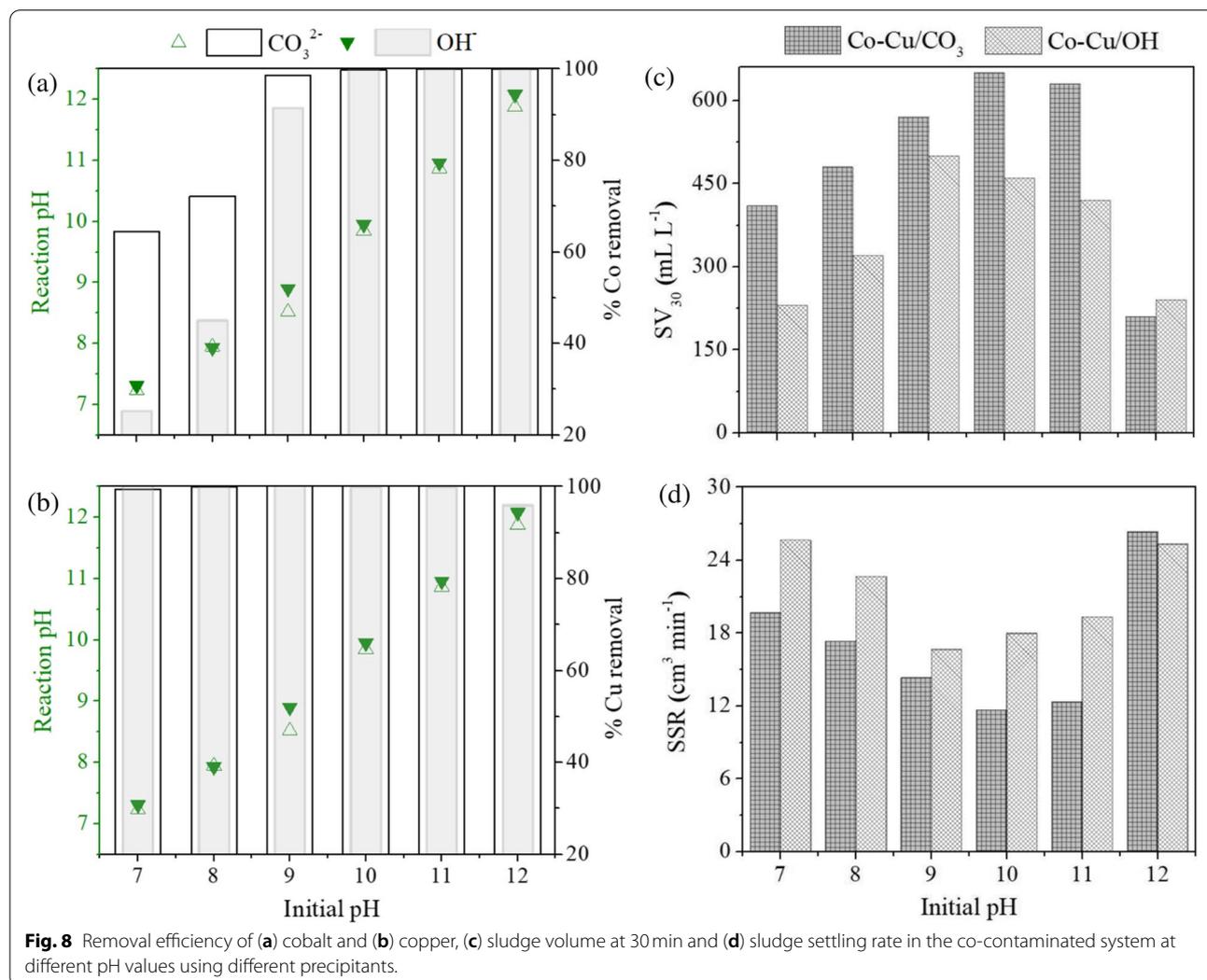
through copper precipitation also depended highly on the solution pH of the reaction system which confirms the dependency of metal co-removal on solution pH [37]. As shown in Fig. 8b, copper was found to be removed easily at all the pH range studied in the co-contaminated system. Copper removal showed a similar trend with that of single copper system. In the co-contaminated system, copper removal also decreased at pH12 possibly due to re-dissolution in the reaction system [42]. It was significantly observed that the co-existence of cobalt did not affect the removal efficiency of copper in the two-component system.

For sodium carbonate precipitant, the SV<sub>30</sub> increased from pH7 to 10 then slightly decreased at pH11. At pH12, a great decrease was observed in Fig. 8c. For hydroxide precipitation, around 200–500 mL L<sup>-1</sup> of SV<sub>30</sub> was observed. The sludge volume generated in the co-contaminated system was observed to be greater than

the single systems of cobalt and copper pollutants at all pH values. This could be associated with the greater total metal concentration, and higher amount of precipitant dosage used to treat two metals in the system. The total metal concentration ( $[M] = [Co] + [Cu]$ ) is about 25.2 mM (12.6 mM Co and 12.6 mM Cu). Thus, the necessary carbonate and hydroxide concentrations also increased probably causing greater sludge volume and slower settleability of precipitates (lower SSR) in the reaction system due to possible trapping of water molecules in the formed precipitates (Fig. 8d) [33]. Higher precipitant dosage as well as higher pH values lead to increase in nucleation number of particles and decrease in particle size, accordingly, causing slower sedimentation time in the precipitation system [9]. The behavior of the precipitates formed is seen to vary at different pH levels for both precipitants used.

### 3.3 Effect of precipitant-to-metal ratio

Based on the crystallization theory, particle nucleation and growth are dependent on the supersaturation level of the solution [43]. Higher saturation level yields greater particle nucleation rate. Precipitant concentration is also significant in the chemical precipitation process. Low precipitant concentration leads to growth of particles on pre-existing solids in the system. On the other hand, high precipitant concentration tends to promote rapid formation of new solid particles leading to increase in the particle number and reduction of the particle size [9]. As the precipitant concentration increases, the precipitant-to-metal ratio also increases. To establish the precipitant-to-metal molar ratio necessary to remove cobalt and copper in the single- and co-contaminated system, several experiments were conducted using 0.5–2.5 M ratios under similar conditions. The highest cobalt removal (98%) was achieved with  $[CO_3^{2-}]/[Co^{2+}]$  ratio of 1.5 with



reaction pH of about 8.5 in the single system as depicted in Fig. 6a. Based on the stoichiometric reaction (Eq. (12)), the carbonate-to-cobalt ratio needed to reach almost complete removal was 50% above the stoichiometric requirement. There was no further increase observed when the  $[CO_3^{2-}]/[Co^{2+}]$  ratio was further increased up to 2.5. On the other hand,  $[OH^-]/[Co^{2+}]$  ratio of 2.0 showed the highest cobalt removal efficiency (84%) at the same reaction pH. This is affirmed from the stoichiometry of the given reaction as Eq. (13). However,  $[OH^-]/[Co^{2+}]$  ratio of 1.5 to 2.5 displayed no significant increase in the reduction of cobalt. Thus,  $[OH^-]/[Co^{2+}]$  ratio of 1.5 was considered as the optimum value to treat cobalt in the single system.

Since the cobalt concentration was set at a specific value, the increase in  $[CO_3^{2-}]/[Co^{2+}]$  molar ratio will lead to a higher  $CO_3^{2-}$  ion concentration. Therefore, this leads to higher supersaturation according to Eq. (29). Moreover, lower radius of critical nucleation is caused by an increase in supersaturation which leads to easier nucleation based on the Gibbs-Thompson equation depicted as Eq. (30) [44]. Accordingly, precipitates with lower particle size will be formed under similar metal content as also mentioned above [39].

$$S = \sqrt{\frac{C_m \cdot C_s}{K_{sp} (ms)}} \tag{29}$$

Where S is supersaturation;  $C_m$  is the concentration of metal ions;  $C_s$  is the precipitant ion concentration;  $K_{sp} (ms)$  is the precipitation solubility product constant.

$$\ln \frac{C}{C_s} = \frac{2\sigma \cdot M}{RT\rho \cdot r_{crit}} \tag{30}$$

Where C is the concentration of the solution,  $C_s$  is the supersaturation,  $\sigma$  is the surface tension, M is the molar mass, R is the thermodynamic constant, T is the thermodynamic temperature,  $\rho$  is the density, and  $r_{crit}$  is the critical radius.

At  $[CO_3^{2-}]/[Co^{2+}]$  of 1.5 to 2.5, the sludge volume did not significantly change as well as the reaction pH (about pH8.5) as shown in Fig. 9 and 10a. It can be deduced that at this range the precipitate formed is of the same species which could possibly be  $Co(OH)_2$  instead of  $CoCO_3$  despite using carbonate system.  $CoCO_3$  might be oxidized to  $Co_3O_4$  followed by reduction to form  $Co(OH)_2$  precipitate [32].  $CoCO_3$  is possibly precipitated at  $[CO_3^{2-}]/[Co^{2+}]$  of 0.5 ( $[CO_3^{2-}] = 6.3\text{mM}$ ) brought about by the moderately alkaline pH (below pH8). 0.5 as  $[CO_3^{2-}]/[Co^{2+}]$  ratio is more than enough to form  $CoCO_3$  in the system based on the calculated necessary  $CO_3^{2-}$  concentration in Section 3.1.1. However, the pH of the solution is still a governing factor in the type of

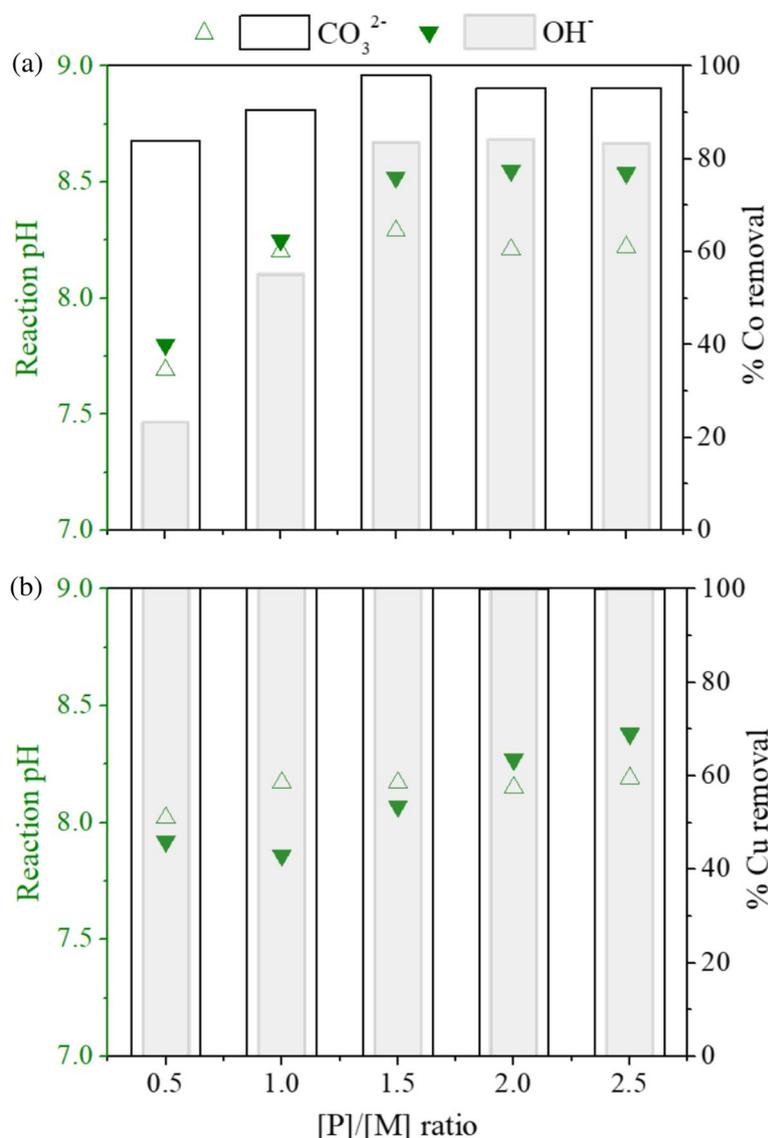
precipitate forming in the reaction system. On the other hand,  $[OH^-]/[Co^{2+}]$  molar ratio of 0.5 produced low sludge volume which might be associated with the low removal efficiency of cobalt in the reaction system.

We can see in Fig. 9b that there was no significant effect observed in the removal of copper under all the  $[P]/[M]$  ratios studied for both precipitants in the study. This might be possibly caused by the pH used in the reaction system (around pH8). The reaction pH for all the studied ratio is in the range of 7.5 to 8.5. This can be affirmed based from the calculated starting pH wherein  $Cu(OH)_2$  and  $CuCO_3$  undergo precipitation. The sludge volume at 30 min was also determined (Fig. 10 a and c) as well as the settling rate of the sludge formed at different  $[P]/[M]$  ratios presented in Fig. 10 b and d. The discrepancies in the sludge volume generated together with the sludge settling rate is possibly affected by the differences in the reaction pH in the single copper system.

For the co-contaminated system, cobalt reached maximum removal at  $[CO_3^{2-}]/[M]$  and  $[OH^-]/[M]$  of 2.0 presented in Fig. 11a. There is no further increase observed when both molar ratios are increased to 2.5. For the single cobalt system,  $[CO_3^{2-}]/[Co^{2+}]$  and  $[OH^-]/[Co^{2+}]$  of 1.5 were found to be the optimal  $[P]/[M]$  conditions which are lower than that of the co-contaminated system. Greater  $[P]/[M]$  ratio is needed to treat cobalt in the co-contaminated system due to the fact this system contains two metals leading to higher supersaturation which makes it harder to precipitate. Moreover, there could be a competition between the cobalt and copper ions to interact with carbonate and hydroxide ions affecting the precipitation efficiency. Similar trend with the single copper system was found for the treatment of copper in the co-contaminated system seen in Fig. 11b. For the carbonate precipitation system,  $[CO_3^{2-}]/[M]$  of 1.0 showed the greatest amount of sludge volume generated. On the other hand,  $[OH^-]/[M]$  of 1.5 generated the largest  $SV_{30}$ .  $SV_{30}$  recorded as observed in Fig. 11c are 450 to 620 and 120 to 500  $mLL^{-1}$  for carbonate and hydroxide precipitants, respectively, greater than that of the single cobalt and copper systems. In both single copper and co-contaminated systems, increasing the  $[P]/[M]$  ratio did not show any significant trend with the settleability of the precipitates in the reaction system depicted in Fig. 10 and 11d. Precipitant-to-metal ratio was found to be at optimum value of 1.2 in the study conducted by Mahasti et al. [45]. In contrary,  $[P]/[M]$  ratio necessary for treatment of cobalt and copper varied for the single- and co-contaminated wastewater stream in this study.

### 3.4 Effect of precipitant type

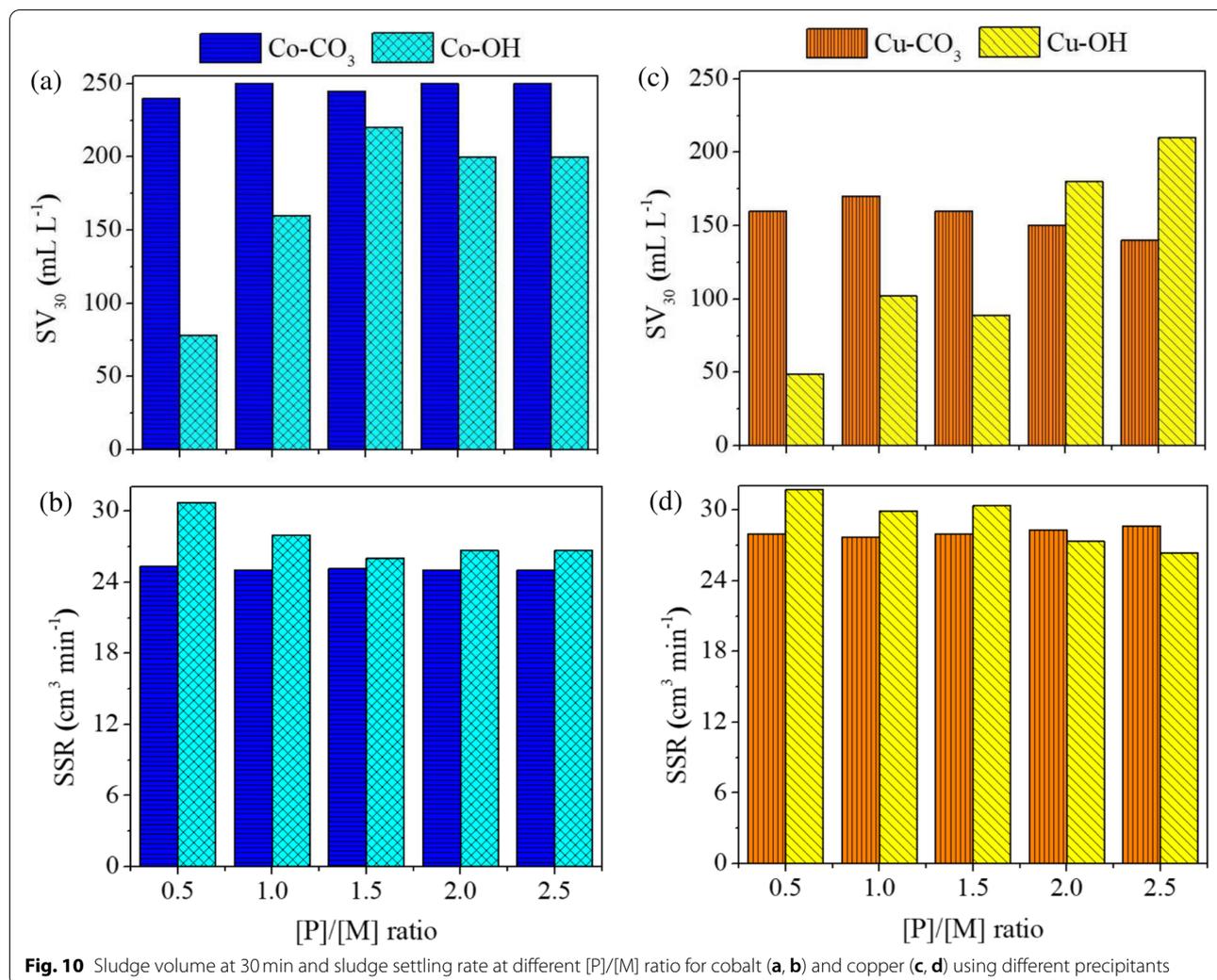
Cobalt removal by carbonate precipitation is significantly higher than that of hydroxide precipitation at



**Fig. 9** Removal efficiency (a) cobalt and (b) copper at different [P]/[M] values using different precipitants (Conditions: [Co]<sub>0</sub> = [Cu]<sub>0</sub> = 12.6 mM; pH = 8; [P]/[M] = variable)

weaker alkaline to neutral conditions in both single- and co-contaminated systems as shown in Fig. 12a. The precipitating agents used for removing cobalt from the simulated wastewater exhibited significant influence on the removal efficiency and resulting sludge in the system. Figure 13 a and b show the supernatant volume for all the systems studied after 30 min of sludge settling. It was also found that the sludge formed by carbonate precipitation exhibits slower settling rate (lower supernatant volume) than that of hydroxide precipitation for all the pH values and [P]/[M] ratio studied for both systems. This may have been caused by less dense sludge

particles and smaller particle size as deduced by Lacson et al. [33]. No general trend was found for the sludge volume formed from single cobalt and single copper systems. The results also show that even at increasing [P]/[M] ratios carbonate precipitation displayed better removal efficiency (lower residual Co) than hydroxide precipitation presented in Fig. 12b. Carbonate precipitation treatment can occur at pH values lower than that of hydroxide precipitation [46] which was evident in this study. Hydroxide system was found to be more effective in reducing the soluble zinc concentration than that of the carbonate system in the study



**Fig. 10** Sludge volume at 30 min and sludge settling rate at different [P]/[M] ratio for cobalt (a, b) and copper (c, d) using different precipitants

conducted by Patterson et al. [46]. Contrarily, carbonate system was found to be more effective and efficient in this study for the treatment of cobalt and copper in single- and co-contaminated streams. In the literature, hydroxide precipitation produces larger volumes of low-density sludge [47]. However, this study observed that the carbonate precipitation led to higher sludge volume than the sludge generated by hydroxide precipitation. When particle recovery and reuse are added advantage, sodium carbonate is also better than sodium hydroxide as precipitant.

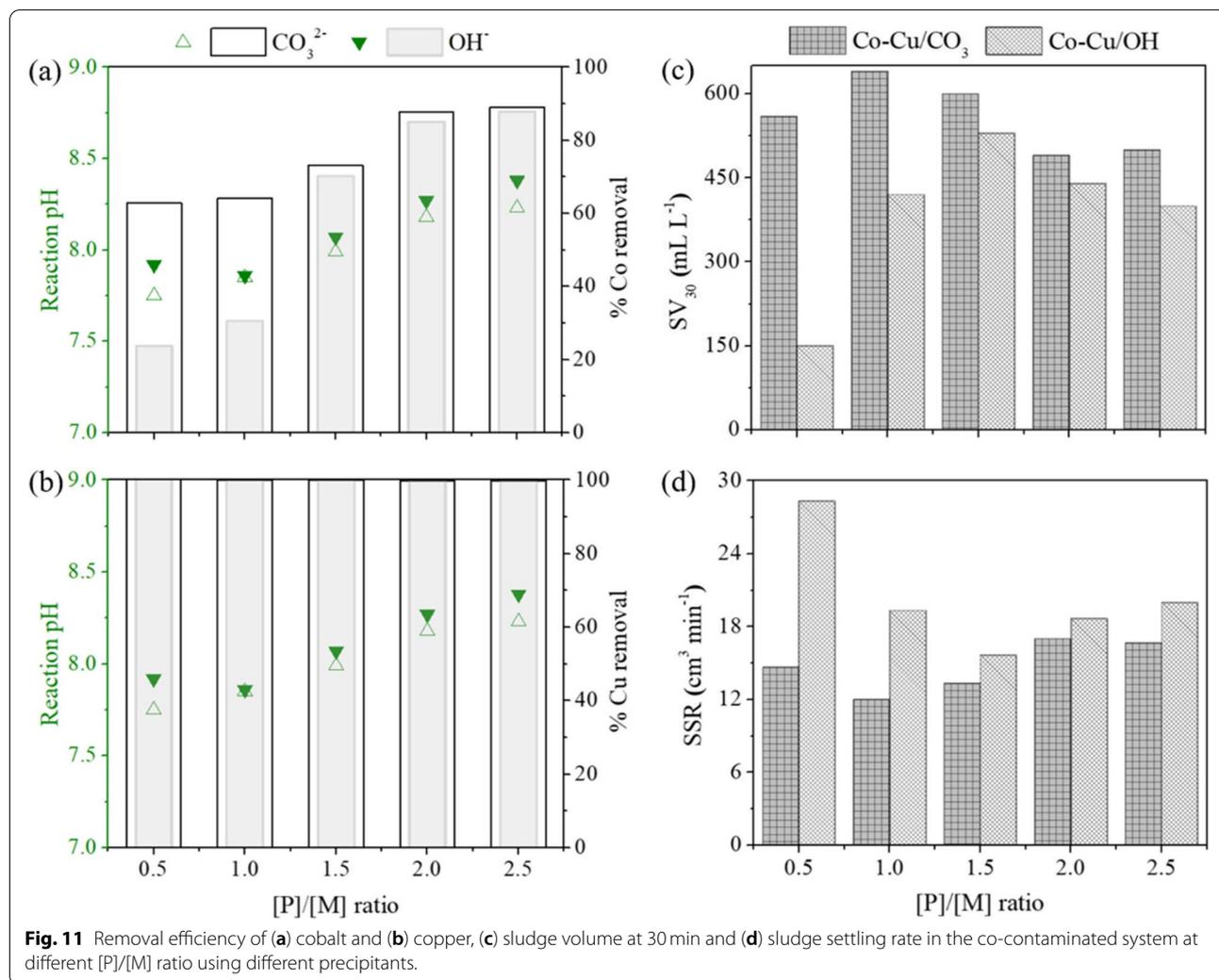
### 3.5 Kinetics of removal

The kinetics of the removal of cobalt and copper were studied under similar conditions (pH8 and [P]/[M] ratio of 1.2) as shown in Fig. 14. The removal rate was

fitted with the pseudo-first order model and the kinetic rate constant,  $k$ , was determined from:

$$\ln\left(\frac{C}{C_0}\right) = kt \tag{31}$$

CoCC and CuCC in Fig. 14 denote the cobalt and copper systems in the Co-Cu/CO<sub>3</sub> system while CoCOH and CuCOH denote the cobalt and copper systems in the Co-Cu/OH system, respectively. It is evident from Fig. 14 a and b that the removal process of copper is significantly faster than that of cobalt for carbonate and hydroxide precipitation under single- and co-contaminated systems. Collins and Kinsela [21] described that Cu<sup>2+</sup> ( $k_{M-H_2O} = 1 \times 10^9 \text{ s}^{-1}$ ) forms precipitates faster than Co<sup>2+</sup> ( $k_{M-H_2O} = 2 \times 10^6 \text{ s}^{-1}$ ) where  $k_{M-H_2O}$  is the characteristic rate constant of water exchange for a metal cation which explains the

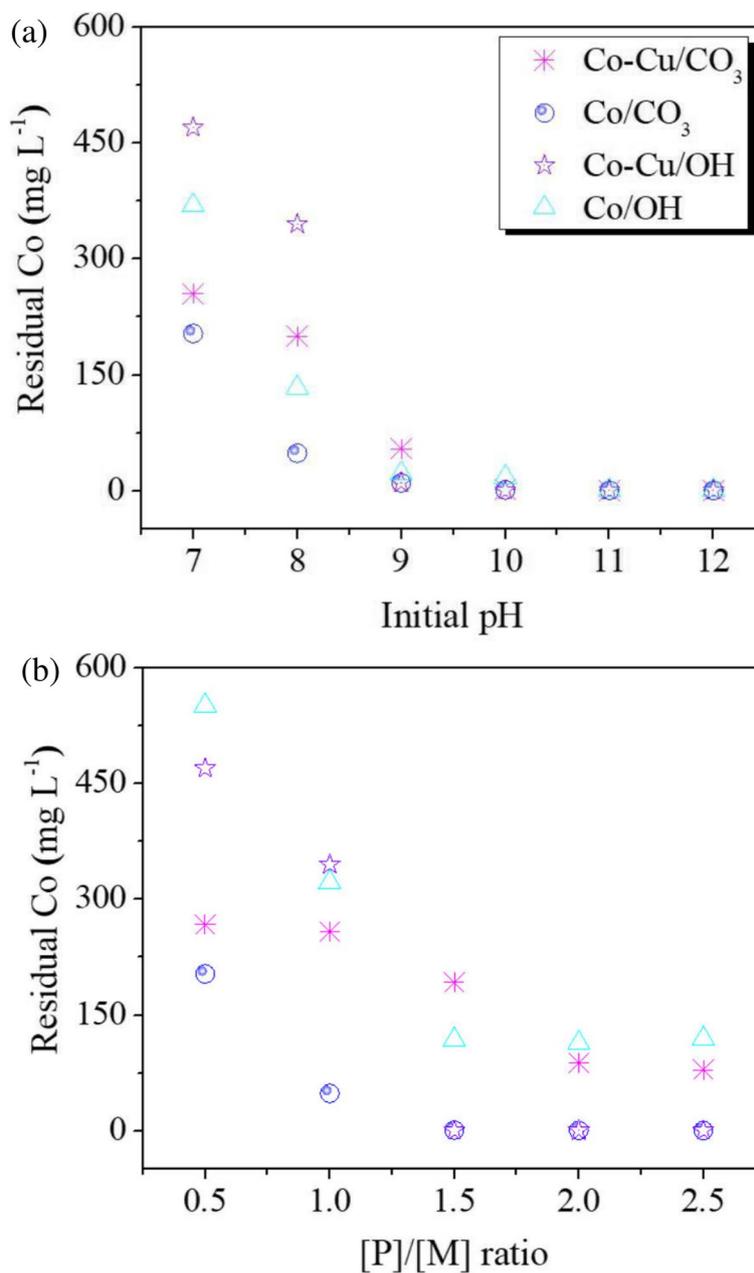


phenomenon occurring for both precipitants in the system as shown in Fig. 14c.

### 3.6 FTIR and EDS analysis

Figure 15 shows the FTIR spectra of all the cobalt and copper precipitates under carbonate and hydroxide single- and co-contaminated systems at pH 10. The chemical changes from precursors to different precipitates were determined. As depicted in the FTIR spectrum of Co/CO<sub>3</sub> system in Fig. 15a, the visible peak centered at 491.3 cm<sup>-1</sup> pertains to the stretching vibrations of Co-O band [48]. The distinctive peak at 480.2 cm<sup>-1</sup> corresponds to Cu-O bonds [49]. The characteristic peak of H-O-H bending vibration at around 1580–1590 cm<sup>-1</sup> which is assigned to a small amount of H<sub>2</sub>O was observed for all the precipitates shown in Fig. 15 a and b. In addition, hydrogen bonded O-H group at the distinctive peak of 3400–3405 cm<sup>-1</sup> and stretching vibration of C-O at distinctive peak of

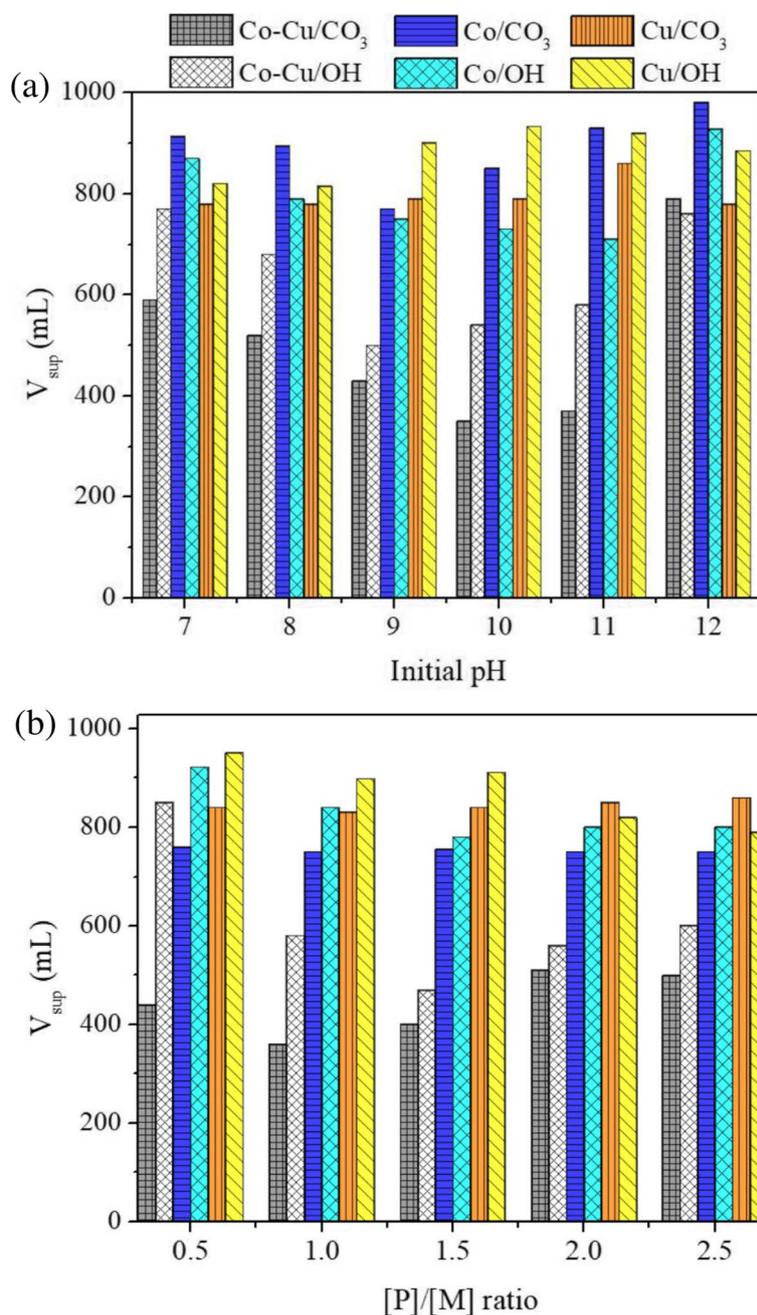
1070–1100 cm<sup>-1</sup> also appeared for all the precipitates formed. The visible peak between 2300 and 2400 cm<sup>-1</sup> is caused by the existence of CO<sub>2</sub> molecule in the air. This characteristic peak also pertains to the C-H stretching vibration. As presented in Fig. 15 b, O -OH bond in Co(OH)<sub>2</sub> centered at about 3600 cm<sup>-1</sup> was observed. Based on Table 2, Co/CO<sub>3</sub> and Cu/CO<sub>3</sub> systems showed that the precipitates formed at pH 10 are CoCO<sub>3</sub> and CuCO<sub>3</sub> based on the atomic percentage determined by EDS analysis. Theoretically, in the Co/CO<sub>3</sub> and Cu/CO<sub>3</sub> systems, both Co and Cu metals should be 20%. Based on the EDS analysis, both metal contents are close to the theoretical metal content (19.9% for Co and 21.7% for Cu). For the co-contaminated system, the theoretical metal content should have a Co to Cu ratio of 1:1 which was also evident from the EDS results for both precipitants. However, for the single Co and single Cu hydroxide systems,



**Fig. 12** Residual cobalt concentrations at different heavy metals systems at different (a) pH values and (b) precipitant-to-metal ratio via carbonate and hydroxide precipitation

the metal content from EDS cannot be exactly compared to the theoretical metal content because of the presence of C and absence of H. Carbon existence is reflected even when it is not initially present in the system. There was also no H detected caused by the non-accuracy of EDS for low atomic number elements. EDS analyses also showed the existence of cobalt and copper in all the precipitates from the single- and

co-contaminated systems which is indicative of the successful precipitation and removal of cobalt and copper from the synthetic electroplating wastewater.

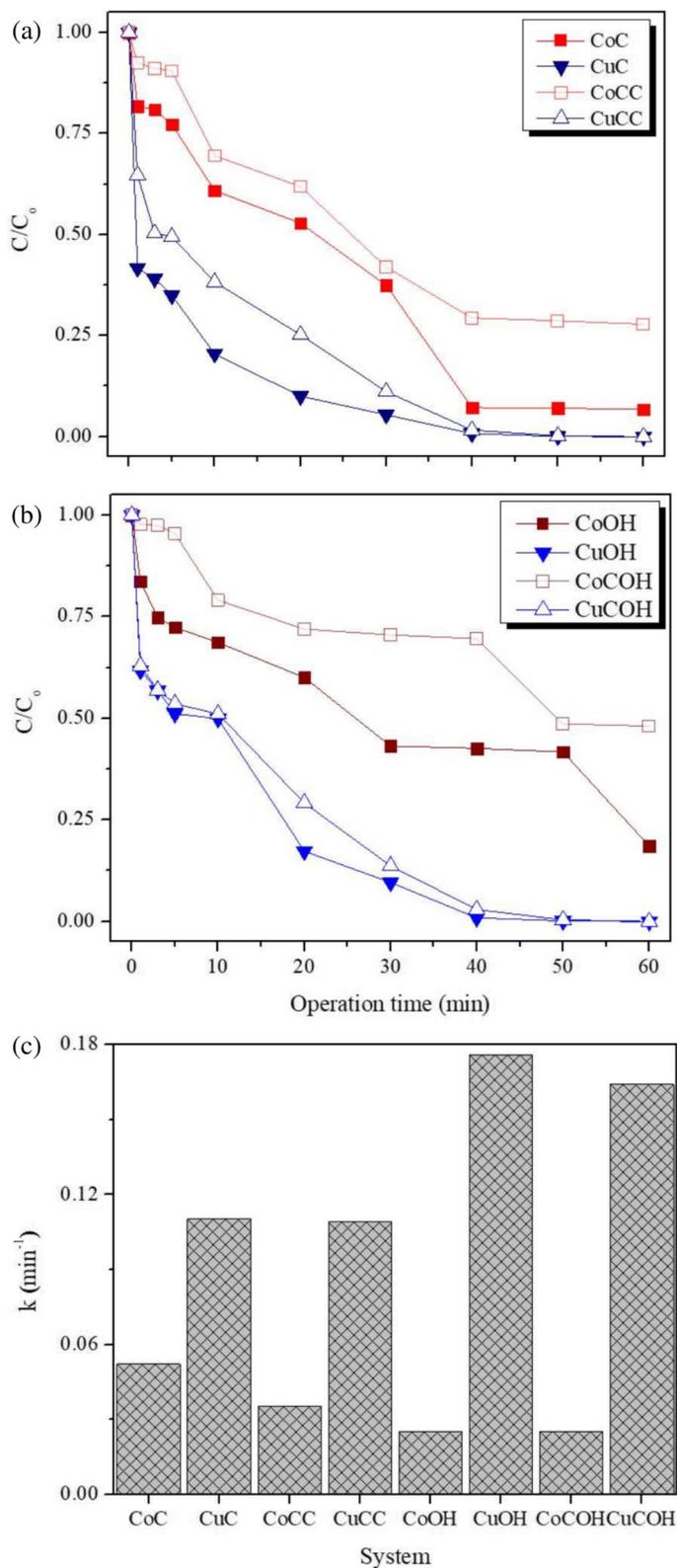


**Fig. 13** Supernatant volume after 30 min under different heavy metals systems at different (a) pH values and (b) precipitant-to-metal ratio via carbonate and hydroxide precipitation

#### 4 Conclusions

The behavior of cobalt in the single- and co-contaminated system showed similar removal at pH value of 10. Copper in the single system was easily removed in the system at pH values of 7–12 which may be due to precipitation-adsorption mechanism at pH values higher than 7.5. Copper probably forms initial copper-bearing

precipitates and the remaining copper in the simulated wastewater stream is adsorbed on the surface of the precipitate formed in the system resulting to its complete removal. Precipitant-to-metal ratio necessary to treat cobalt varied for the single- and co-contaminated systems for both precipitants used. For the single cobalt system, the [P]/[M] for both carbonate and hydroxide



**Fig. 14** (a, b) Removal of cobalt and copper and (c) kinetic rate constant for both precipitant systems

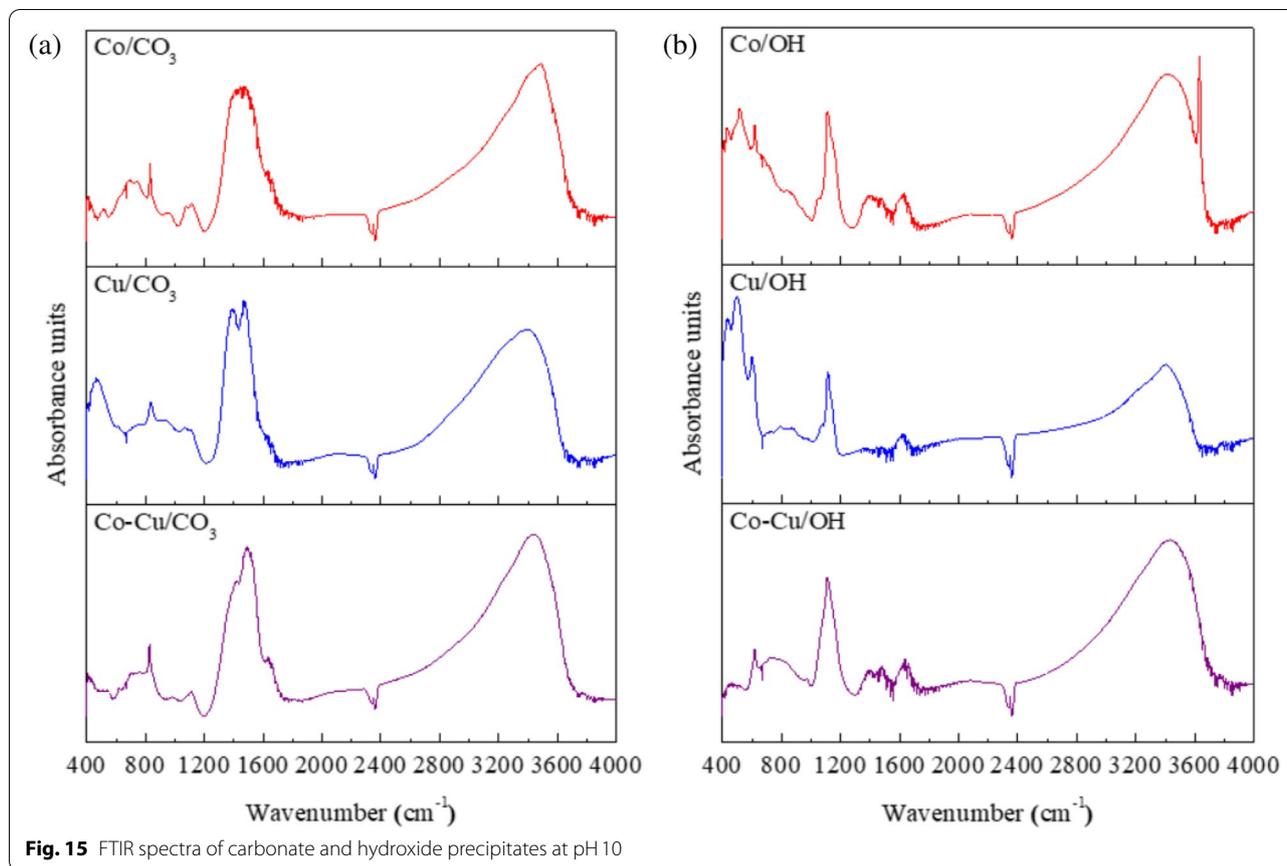


Fig. 15 FTIR spectra of carbonate and hydroxide precipitates at pH 10

Table 2 EDS analysis (atomic %) of precipitates at pH 10

System	Co (%)	Cu (%)	C (%)	O (%)
Co/CO <sub>3</sub>	19.9	–	20.7	59.4
Cu/CO <sub>3</sub>	–	21.7	23.2	55.1
Co-Cu/CO <sub>3</sub>	11.0	12.6	14.7	59.7
CoOH	25.1	–	10.6	64.3
CuOH	–	31.7	16.1	52.3
Co-Cu/OH	12.2	13.2	11.1	63.4

precipitants is 1.5. On the other hand, higher [P]/[M] to treat Co for the co-contaminated system was observed at a value of 2.0 for both precipitants. There was no significant effect on the copper system possibly due to excess precipitant dosage. The co-existence of copper did not significantly affect the removal of cobalt in the co-contaminated wastewater stream. Carbonate and hydroxide precipitation systems are effective treatment methods in dealing with the metal pollutants contained in electroplating wastewater leading to high removal efficiency. In addition, carbonate precipitation was found to be a more effective and efficient treatment alternative to

hydroxide precipitation, and soluble cobalt and copper can be removed from the wastewater streams using soda ash. One of the advantages of carbonate system with the hydroxide system was the operation at lower pH values typically around 7–8. In terms of sludge volume, carbonate system had added advantage when the additional target is particle recovery and reuse.

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**Authors' contributions**

Khyle Glainmer N. Quiton conceptualized the study and carried out the experimental studies. Ming-Chun Lu provided conceptual and technical guidance for all the aspects of the work. Yao-Hui Huang commented, reviewed, and approved its completion. All authors read and approved the final manuscript.

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**Availability of data and materials**

All data generated or analyzed in this work are available from the corresponding author on reasonable request.

## Declarations

### Competing interests

The authors declare that they have no known competing financial interests.

### Author details

<sup>1</sup>Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan. <sup>2</sup>Sustainable Environment Research Center, National Cheng Kung University, Tainan 70101, Taiwan. <sup>3</sup>Department of Environmental Engineering, National Chung Hsing University, Taichung 40227, Taiwan.

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## References

- Qiu BB, Tao XD, Wang H, Li WK, Ding X, Chu HQ. Biochar as a low-cost adsorbent for aqueous heavy metal removal: a review. *J Anal Appl Pyroly.* 2021;155:105081.
- Zbair M, Anfar Z, Ahsaine HA. Reusable bentonite clay: modelling and optimization of hazardous lead and *p*-nitrophenol adsorption using a response surface methodology approach. *RSC Adv.* 2019;9:5756–69.
- Saad DR, Alismaeel ZT, Abbar AH. Cobalt removal from simulated wastewaters using a novel flow-by fixed bed bio-electrochemical reactor. *Chem Eng Process.* 2020;156:108097.
- Godiya CB, Cheng X, Li DW, Chen Z, Lu XL. Carboxymethyl cellulose/polyacrylamide composite hydrogel for cascaded treatment/reuse of heavy metal ions in wastewater. *J Hazard Mater.* 2019;364:28–38.
- Sharma AK, Priya, Kaith BS, Singh A, Isha, Vipula, et al. Enzymatic construction of quinine derivative of dextrin/PVA based hybrid gel film for the simultaneous detection and removal of copper and lead ions in real water samples. *Chem Eng J.* 2020;382:122891.
- Awual MR, Hasan MM, Islam A, Asiri AM, Rahman MM. Optimization of an innovative composited material for effective monitoring and removal of cobalt(II) from wastewater. *J Mol Liq.* 2020;298:112035.
- Liu HL, Cui SQ, Shi F, Pu SZ. A diarylethene based multi-functional sensor for fluorescent detection of  $\text{Cd}^{2+}$  and colorimetric detection of  $\text{Cu}^{2+}$ . *Dyes Pigments.* 2019;161:34–43.
- Zbair M, Ahsaine HA, Anfar Z, Slassi A. Carbon microspheres derived from walnut shell: rapid and remarkable uptake of heavy metal ions, molecular computational study and surface modeling. *Chemosphere.* 2019;231:140–50.
- Chen QY, Yao Y, Li XY, Lu J, Zhou J, Huang ZL. Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. *J Water Process Eng.* 2018;26:289–300.
- Duan CY, Ma TY, Wang JY, Zhou YB. Removal of heavy metals from aqueous solution using carbon-based adsorbents: a review. *J Water Process Eng.* 2020;37:101339.
- Junuzovic H, Begic S, Selimovic A, Dozic A, Cvrk R, Ahmetovi M. Efficiency of carbonate precipitation and removal of copper and nickel ions from their monocomponent and two-component aqueous solutions. *Int J Res Appl Sci Biotechnol.* 2019;06:11–5.
- Wolowicz M, Komorowska-Kaufman M, Pruss A, Rzepa G, Bajda T. Removal of heavy metals and metalloids from water using drinking water treatment residuals as adsorbents: a review. *Minerals-Basel.* 2019;9:487.
- Oustadakis P, Agatzini-Leonardou S, Tsakiridis PE. Nickel and cobalt precipitation from sulphate leach liquor using MgO pulp as neutralizing agent. *Miner Eng.* 2006;19:1204–11.
- Djoudi N, Mostefa ML, Muhr H. Precipitation of cobalt salts for recovery in leachates. *Chem Eng Technol.* 2019;42:1492–9.
- Pang FM, Teng SP, Teng TT, Omar AKM. Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions. *Water Qual Res J Can.* 2009;44:174–82.
- Awual MR, Yaita T, Okamoto Y. A novel ligand based dual conjugate adsorbent for cobalt(III) and copper(II) ions capturing from water. *Sensor Actuat B-Chem.* 2014;203:71–80.
- Abdullah N, Yusof N, Lau WJ, Jaafar J, Ismail AF. Recent trends of heavy metal removal from water/wastewater by membrane technologies. *J Ind Eng Chem.* 2019;76:17–38.
- Ghorpade A, Ahammed MM. Water treatment sludge for removal of heavy metals from electroplating wastewater. *Environ Eng Res.* 2018;23:92–8.
- Lacson CFZ, Lu MC, Huang YH. Chemical precipitation at extreme fluoride concentration and potential recovery of  $\text{CaF}_2$  particles by fluidized-bed homogenous crystallization process. *Chem Eng J.* 2021;415:128917.
- Huang JH, Kargl-Simard C, Oliazadeh M, Alfantazi AM. pH-controlled precipitation of cobalt and molybdenum from industrial waste effluents of a cobalt electrodeposition process. *Hydrometallurgy.* 2004;75:77–90.
- Collins RN, Kinsela AS. The aqueous phase speciation and chemistry of cobalt in terrestrial environments. *Chemosphere.* 2010;79:763–71.
- Cuppert JD, Duncan SE, Dietrich AM. Evaluation of copper speciation and water quality factors that affect aqueous copper tasting response. *Chem Senses.* 2006;31:689–97.
- Popenda A. Effect of redox potential on heavy metals and As behavior in dredged sediments. *Desalin Water Treat.* 2014;52:3918–27.
- Duckworth OW, Bargar JR, Jarzecki AA, Oyerinde O, Spiro TG, Sposito G. The exceptionally stable cobalt(III)-desferrioxamine B complex. *Mar Chem.* 2009;113:114–22.
- Cosovic B, Degobbi D, Bilinski H, Branica M. Inorganic cobalt species in seawater. *Geochim Cosmochim Acta.* 1982;46:151–8.
- Du HM, Jiao LF, Wang QH, Huan QN, Guo LJ, Si YC, et al. Morphology control of  $\text{CoCO}_3$  crystals and their conversion to mesoporous  $\text{Co}_3\text{O}_4$  for alkaline rechargeable batteries application. *Cryst Eng Comm.* 2013;15:6101–9.
- Boguta P, Sokolowska Z. Zinc binding to fulvic acids: assessing the impact of pH, metal concentrations and chemical properties of fulvic acids on the mechanism and stability of formed soluble complexes. *Molecules.* 2020;25:1297.
- Al-Shahrani SS. Treatment of wastewater contaminated with cobalt using Saudi activated bentonite. *Alexandria Eng J.* 2014;53:205–11.
- Qasem NAA, Mohammed RH, Lawal DU. Removal of heavy metal ions from wastewater: a comprehensive and critical review. *Npj Clean Water.* 2021;4:36.
- Guo MM, Xi XL, Li S, Li CW, Nie ZR, Xu KH. Preparation of small-particle and high-density cobalt carbonate using a continuous carbonate precipitation method and evaluation of its growth mechanism. *Materials.* 2019;12:3394.
- Wu QD, Liu S, Yao SM, Gao XP. Electrochemical performance of cobalt hydroxide carbonate nanorods. *Electrochem Solid St.* 2008;11:A215–8.
- Lin SN, Niu LP, Pan XJ, Liang ZP, Zhang TA. Study on preparation and recovery of cobalt hydroxide and cobalt carbonate. *Hydrometallurgy.* 2021;203:105518.
- Lacson CFZ, Lu MC, Huang YH. Fluoride-rich wastewater treatment by ballast-assisted precipitation with the selection of precipitants and discarded or recovered materials as ballast. *J Environ Chem Eng.* 2021;9:105713.
- Sun JM, Huang JC. Co-removal of hexavalent chromium through adsorption during copper precipitation. *Water Sci Technol.* 2004;50:201–8.
- Marchioretto MM, Bruning H, Rulkens W. Heavy metals precipitation in sewage sludge. *Sep Sci Technol.* 2005;40:3393–405.
- Sun JM, Zhao XH, Huang JC. Characterization of adsorbent composition in co-removal of hexavalent chromium with copper precipitation. *Chemosphere.* 2005;58:1003–10.
- Sun JM, Chang SY, Li R, Huang JC. Factors affecting co-removal of chromium through copper precipitation. *Sep Purif Technol.* 2007;56:57–62.
- Sanchez MP, Barrera M, Gonzalez S, Souto RM, Salvarezza RC, Arvia AJ. Electrochemical behavior of copper in aqueous moderate alkaline media, containing sodium carbonate and bicarbonate, and sodium perchlorate. *Electrochim Acta.* 1990;35:1337–43.
- Guo MM, Xi XL, Li S, Long XL, Nie ZR, Xu KH. A novel liquid precipitation route to synthesize high-quality cobalt carbonate with low chloride ions concentration. *IOP C Ser Earth Env.* 2019;295:032104.
- Phiwidang K, Suphankij S, Mekprasart W, Pecharapa W. Synthesis of CuO nanoparticles by precipitation method using different precursors. *Engy Proced.* 2013;34:740–5.
- Safitri N, Mubarak MZ, Winarko R, Tanlega Z. Recovery of nickel and cobalt as MHP from limonitic ore leaching solution: kinetics analysis and precipitate characterization. *AIP Conf Proc.* 2018;1964:020030.
- Le VG, Vo DVN, Nguyen NH, Shih YJ, Vu CT, Liao CH, et al. Struvite recovery from swine wastewater using fluidized-bed homogeneous granulation process. *J Environ Chem Eng.* 2021;9:105019.

43. Lutsko JF. How crystals form: a theory of nucleation pathways. *Sci Adv.* 2019;5:eaav7399.
44. Thanh NTK, Maclean N, Mahiddine S. Mechanisms of nucleation and growth of nanoparticles in solution. *Chem Rev.* 2014;114:7610–30.
45. Mahasti NNN, Shih YJ, Huang YH. Removal of iron as oxyhydroxide (FeOOH) from aqueous solution by fluidized-bed homogeneous crystallization. *J Taiwan Inst Chem E.* 2019;96:496–502.
46. Patterson JW, Allen HE, Scala JJ. Carbonate precipitation for heavy metals pollutants. *J Water Pollut Con F.* 1977;49:2397–410.
47. Fu FL, Wang Q. Removal of heavy metal ions from wastewaters: a review. *J Environ Manage.* 2011;92:407–18.
48. Wang SL, Wang RH, Chang J, Hu N, Xu CH. Self-supporting  $\text{Co}_3\text{O}_4$ /graphene hybrid films as binder-free anode materials for lithium ion batteries. *Sci Rep-UK.* 2018;8:3182.
49. Ethiraj AS, Kang DJ. Synthesis and characterization of CuO nanowires by a simple wet chemical method. *Nanoscale Res Lett.* 2012;7:70.

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